



Electrolytic cell containing different groups of ions with anomalous diffusion approach



F.R.G.B. Silva^a, R. Rossato^{a,b}, E.K. Lenzi^{a,c,*}, R.S. Zola^{a,b}, H.V. Ribeiro^{a,b}, M.K. Lenzi^d, G. Gonçalves^e

^a Departamento de Física, Universidade Estadual de Maringá, Avenida Colombo 5790, 87020-900 Maringá, PR, Brazil

^b Departamento de Física, Universidade Tecnológica Federal do Paraná, Rua Marçílio Dias 635, 86812-460 Apucarana, PR, Brazil

^c Departamento de Física, Universidade Estadual de Ponta Grossa, Av. General Carlos Cavalcanti 4748, 84030-900 Ponta Grossa, PR, Brazil

^d Departamento de Engenharia Química, Universidade Federal do Paraná, 81531-990 Curitiba, PR, Brazil

^e Departamento de Engenharia Química, Universidade Tecnológica Federal do Paraná, Ponta Grossa 84016-210, PR, Brazil

ARTICLE INFO

Article history:

Received 11 October 2014

Received in revised form 19 March 2015

Accepted 19 March 2015

Available online 20 March 2015

Keywords:

Anomalous diffusion

Electrical response

Impedance

ABSTRACT

The electrical response of an electrolytic cell containing more than one group of ions is investigated under the fractional approach where integro – differential boundary conditions and fractional time derivative of distributed order are considered. The model derived here, which accounts for anomalous diffusion of charges in a dielectric media, is compared with experimental data for mixtures of two salts with same valence and water and a good agreement was found. We show that in the low frequency limit, the electrical response is essentially governed by the boundary conditions and suppress the formation of a second plateau predicted when surface effects are neglected, being therefore linked to an anomalous diffusive process which, in the usual circuit description, may be connected to constant phase elements. Our model may be important for the interpretation of ionic density measurements in liquid crystals and other electrolytic cells in a more realistic fashion.

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1. Introduction

Comprehending the electrical response is an important issue since it plays a major role on the mechanism, kinetics, and thermodynamics of various physicochemical processes. In this context, the impedance spectroscopy [1] is an experimental technique of great popularity for analyzing the response of a system subjected to an external, usually of small amplitude, and periodic current signal. The results obtained via this technique have been investigated, in general, by the Poisson–Nernst–Planck (PNP) model and/or equivalent circuits. However, the behavior exhibited experimentally often deviate from what is obtained by the standard formalism, where the impedance Z assumes the asymptotic behavior $Z \sim 1/(i\omega)$ in the low frequency limit presented by the PNP model. This disagreement between experimental data and usual models is a strong motivation for considering changes in the usual description. One of them is concerned to the diffusive motion of the ions, which can be extended to anomalous diffusion, for instance, via fractional derivatives [2] or by generalizing the

boundary conditions [3] due to the complexity of the surface effects. In fact, different scenarios have been considered with the fractional approach [4–7], including the description of electrolytic cells [8] with integro-differential boundary conditions (PNPA model) [9] taking into account surface effects that may lead to anomalous behavior such as the adsorption–desorption phenomena. The PNPA model has also been used to show that anomalous diffusion can indeed provide a new perspective to the investigation of electrical response [10,11], and that it can be connected with equivalent circuits with constant phase elements [12], having however, a deeper physical meaning. It is worth to point out that, electric circuits play an important role in the context of the electrical response. In particular, several arrangements of equivalent circuits have been proposed in agreement to experimental scenarios. An example is the Randles circuit [13] that consists of a resistance in series with a parallel combination of a double-layer capacitance and an impedance of a faradaic reaction which is also modified by incorporating constant phase elements. A detailed discussion about the various distributed circuit elements that can be incorporated into equivalent circuits was presented in Refs. [14–16]. However, as discussed in Ref. [17], it is necessary a careful analysis before reaching general conclusions about the data, since the incorrect choice of the equivalent circuit can lead to deceptive conclusions about the process that occurs in the cell.

* Corresponding author at: Departamento de Física, Universidade Estadual de Ponta Grossa, Av. General Carlos Cavalcanti 4748, 84030-900 Ponta Grossa, PR, Brazil.

E-mail address: eklenzi@dfi.uem.br (E.K. Lenzi).

Our goal is to investigate a PNPA model by considering more than one group of ions. Such study is of great importance for electrolytic cells, such as fuel cells. In particular, liquid crystal cells and displays need to deal with ionic impurities, an undesirable sub-product. It is often necessary to determine the concentration of ions through impedance measurements. Nonetheless, most of the models available do not deal with the reality, which is, to consider more than one ionic impurity, nor do they completely describe the surface effects associated to the confining substrates, all of which contribute to unwelcome characteristics such as low voltage holding ratio. Indeed, generalizations of the PNP model considering different groups of ions have been analyzed before [18–20], but, as discussed above, this approach cannot predict the experimental behavior correctly, specially in the low frequency regime where surface phenomena govern the dynamics. In this article, a model in the PNPA framework considering different groups of ions as well as their valances is reported and compared with experimental data obtained from measuring the impedance spectrum of the mixture of two salts in Milli-Q water: NH_4Cl and KClO_3 (both monovalent) $\text{CdCl}_2 \cdot 2\text{H}_2\text{O}$ and HgCl_2 (both bivalent) in a dilute solutions.

2. The model

Let us introduce an extension of the model proposed in Refs. [9–11] by considering the presence of different groups of positive ($\alpha = +$) and negative ($\alpha = -$) ions in an electrolytic cell of thickness d with electrodes placed at $z = \pm d/2$ of a Cartesian reference frame where z is normal to the electrodes. Thus, we consider the following fractional diffusion equation of distributed order for the bulk densities of ions ($n_{\alpha l}$) in presence of reaction terms $\Lambda_{\alpha l}(t)$

$$\int_0^1 d\gamma' \tau(\gamma') \frac{\partial^{\gamma'}}{\partial t^{\gamma'}} n_{\alpha l}(z, t) = -\frac{\partial}{\partial z} J_{\alpha l}(z, t) - \int_{t_0}^t \Lambda_{\alpha l}(t-t') n_{\alpha l}(z, t') dt'. \quad (1)$$

where $\tau(\gamma')$ correspond to a distribution of γ' . Note that depending on the choice of $\tau(\gamma')$ different situations may be recovered such as the the fractional diffusion equation for $\tau(\gamma') \propto \delta(\gamma' - \gamma)$ for $0 < \gamma < 1$, situations characterized by different regimes [21], e.g., $\tau(\gamma') \propto \delta(\gamma' - \gamma) + \tau' \delta(\gamma' - 1)$, $\tau(\gamma') \propto \gamma'^{k-1}$ ultraslow diffusion [22], and for $\tau(\gamma') \propto \delta(\gamma' - 1)$ the usual diffusion is recovered. The current density is given by

$$J_{\alpha l}(z, t) = -\mathcal{D}_{\alpha l} \frac{\partial}{\partial z} n_{\alpha l}(z, t) \mp \frac{q_l \mathcal{D}_{\alpha l}}{k_B T} n_{\alpha l}(z, t) \frac{\partial}{\partial z} V(z, t). \quad (2)$$

In Eq. (2), $\mathcal{D}_{\alpha l}$ and q_l are the diffusion coefficient and the ionic charge of the group l ; V is the actual electric potential across a sample, k_B is the Boltzmann constant, and T is absolute temperature. The effective time-dependent potential across the sample is determined by the Poisson's equation

$$\frac{\partial^2}{\partial z^2} V(z, t) = -\frac{1}{\varepsilon} \sum_{l=1}^N q_l (n_{+l}(z, t) - n_{-l}(z, t)). \quad (3)$$

In Eq. (3), the dielectric coefficient ε is measured in ε_0 units and N represents the number of different group of ions. We consider that Eq. (1) is subjected to the boundary condition [3,9]

$$J_{\alpha l}\left(\pm \frac{d}{2}, t\right) = \pm \int_0^1 d\vartheta \int_{t_0}^t d\bar{t} \bar{k}_{\alpha l}(t-\bar{t}, \vartheta) \frac{\partial^{\vartheta}}{\partial \bar{t}^{\vartheta}} n_{\alpha l}\left(\pm \frac{d}{2}, \bar{t}\right). \quad (4)$$

The fractional time derivative considered here, in Eqs. (1) and (4), is the Caputo one, given by:

$$\frac{\partial^{\mu}}{\partial t^{\mu}} n_{\alpha l}(z, t) = \frac{1}{\Gamma(1-\mu)} \int_{t_0}^t dt' \frac{n'_{\alpha l}(z, t')}{(t-t')^{\mu}}, \quad (5)$$

with $0 < \mu < 1$ and $n'_{\alpha l}(z, t) \equiv \partial_t n_{\alpha l}(z, t)$. Notice this is one of the possible approaches for anomalous diffusion, others scenarios can be found in Ref. [21]. We consider, in Eqs. (1), (4), and (5), $t_0 \rightarrow -\infty$ which as discussed in Ref. [23] is suitable choice to analyze the response of the system to a periodic applied potential like the one to be consider here.

Eq. (4) recovers several situations such as the blocking electrodes for $k_{\alpha l}(t, \vartheta) = 0$ ($J_{\alpha l}(z, t)|_{z=\pm d/2} = 0$), adsorption-desorption process at the surfaces corresponding to the Henry approximation (linear kinetic equation of first order) when $k_{\alpha l}(t, \vartheta) \propto e^{-t/\tau} \delta(\vartheta - 1)$, and the Chang-Jaffe condition for $k_{\alpha l}(t, \vartheta) \propto \delta(t) \delta(\vartheta)$ ($J_{\alpha l}(z, t)|_{z=\pm d/2} = \pm k n_{\alpha l}(z, t)|_{z=\pm d/2}$). In this manner, Eq. (4) provides an unified framework for dealing with several boundary conditions and also the non-usual relaxations [24] which emerge when $k_{\alpha l}(t, \vartheta) = \bar{\tau}(\vartheta) \kappa(t)$ for a ϑ distribution $\bar{\tau}(\vartheta)$ and $\kappa(t)$ arbitrarities.

The previous set of equations represent a general model for an electrolytic cell containing different groups of ions from which is possible to obtain an analytical solution in the linear approximation for the stationary state and the electrical impedance, as we shall present in the next section.

2.1. Linear approximation

In the linear approximation (small a.c. signal limit), one can consider that $n_{\alpha l}(z, t) = \mathcal{N}_l + \delta n_{\alpha l}(z, t)$, with $\mathcal{N}_l \gg |\delta n_{\alpha l}(z, t)|$, which states that, in the low-voltage regime, the densities differ only slightly from the zero field densities, where \mathcal{N}_l represents the number of ions. In addition, we also consider $\delta n_{\alpha l}(z, t) = \eta_{\alpha l}(z) e^{i\omega t}$ to analyze the impedance when the electrolytic cell is subjected to a time dependent potential $V(z, t) = \phi(z) e^{i\omega t}$, with $V(\pm d/2, t) = \pm V_0 e^{i\omega t}/2$. We also assume that, in each group, the positive and negative ions have the same mobility, i.e., the diffusion coefficients for positive and negative ions of the same group are equal. This assumption avoids cumbersome calculations since the diffusion coefficients are, for the experimental situations analyzed, very similar. The substitution of these expressions into Eqs. (1), (3), and (4) yields a set of coupled equations which may be simplified by using the auxiliary functions $\psi_{\pm l}(z) = \eta_{+l} \pm \eta_{-l}$, where $\psi_{\pm l}$ are solutions of the differential equations

$$\frac{d^2}{dz^2} \psi_{+l} - 2 \frac{\mathcal{N}_l}{\mathcal{D}_l} \mathcal{I}_l = \Phi_l(i\omega) \psi_{+l} \quad (6)$$

$$\frac{d^2}{dz^2} \psi_{-l} - \sum_{k=1}^N \frac{q_k}{q_l \lambda_l^2} \psi_{-k} = \Phi_l(i\omega) \psi_{-l} \quad (7)$$

where $\Phi_l(i\omega) = \Psi_l(i\omega) + \Lambda_l(i\omega)/\mathcal{D}_l$, $\Psi_l(i\omega) = (1/\mathcal{D}_l) \int_0^1 d\gamma' \tau(\gamma') (i\omega)^{\gamma'}$, $\Lambda_l(i\omega) = \int_0^1 d\bar{t} \Lambda_l(\bar{t}) e^{i\omega \bar{t}}$, $\mathcal{I}_l = \int_0^{\infty} dv \Lambda_l(v)$, and $\lambda_l = \sqrt{\varepsilon k_B T / (2 \mathcal{N}_l q_l^2)}$ is the Debye screening length. In this scenario, the boundary conditions are given by

$$\frac{d}{dz} \psi_{-l} + 2 \frac{q_l \mathcal{N}_l}{k_B T} \frac{d}{dz} \phi \Big|_{z=\pm d/2} = \mp \Upsilon_l(i\omega) \psi_{-l} \Big|_{z=\pm d/2}, \quad (8)$$

$$\frac{d}{dz} \psi_{+l} \Big|_{z=\pm d/2} = \mp \Upsilon_l(i\omega) \psi_{+l} \Big|_{z=\pm d/2}, \quad (9)$$

with $\Upsilon_l(i\omega) = (1/\mathcal{D}_l) \int_0^1 d\vartheta (i\omega)^{\vartheta} \int_0^{\infty} dt' k_{\alpha l}(t', \vartheta) e^{i\omega t'}$.

2.2. Predictions

We consider, for simplicity, the previous system of equations for two group of ions with $q_1 = q_2 = q$, i.e., the same charge, and focus our attention in $\psi_{-l}(z)$ and $\phi(z)$ from which the impedance

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